



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 289 077
A2**

EUROPEAN PATENT APPLICATION

Application number: 88200744.6

Int. Cl.4: **C08K 5/13 , C08L 73/00 ,
/(C08L73/00,C08K5:13)**

Date of filing: 19.04.88

Priority: 29.04.87 GB 8710171

Date of publication of application:
02.11.88 Bulletin 88/44

Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

Applicant: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

Inventor: **Schmitter, André, Dr.**
7 Rue des Alpes
F-68220 Hegenheim(FR)

Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague(NL)

Thermostabilized copolymer composition.

A stabilized composition comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and, based on the weight of the copolymer, from 0.03 to 5.0 %w to an additive selected from phenolic dicarboxylates, and phenolic dicarboxamides, optionally together with phenolic phosphites.

EP 0 289 077 A2

THERMOSTABILIZED COPOLYMER COMPOSITION

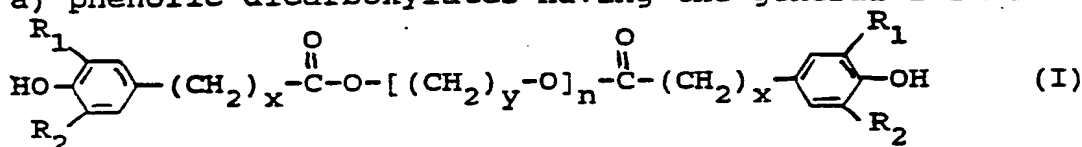
The present invention relates to copolymer compositions comprising certain additives. The relevant copolymers are characterized by having an alternating structure $[A-CO]_n$ in which A is a unit derived from an olefinically unsaturated compound. The term "copolymer" includes terpolymers in which different units A are present. As an example of suitable terpolymers reference is made to a copolymer of ethylene, carbon monoxide and propylene or butylene.

The relevant alternating copolymers and their methods of preparation are known per se, cf US-A 3 694 412, EP-A 121 965 and EP-A 181 014. Whilst these copolymers have attractive physical and mechanical properties such as yield stress, tensile strength, impact strength and flexural modulus, their processing stability and long-life or end-use stability leave room for improvement.

Applicants have found that a very large number of commercial thermostabilizers that perform well in polyamides, polyolefins, polyacrylates, polystyrenes and various other commodity thermoplastics and engineering thermoplastics fail to achieve adequate thermostabilization of alternating ethylene/carbon monoxide copolymers. It is therefore surprising to find that a few small groups of narrowly defined additives have been found that do produce the desired thermostabilizing improvement.

The present invention provides stabilized copolymer compositions comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and from 0.03 to 5.0 %w of an additive selected from

a) phenolic dicarboxylates having the general formula



in which

x is 0 to 4, preferably 2

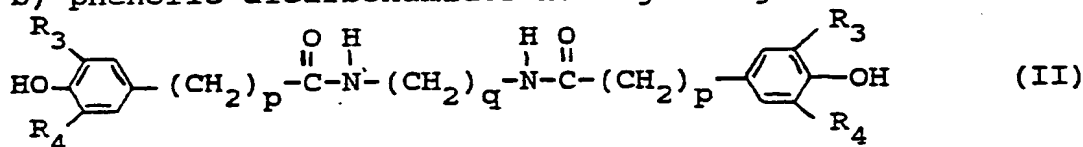
y is 2 to 6, preferably 2 or 3

n is 2 to 8, preferably 3

R₁ is hydrogen or alkyl with 1 to 6 carbon atoms

R₂ is alkyl with 1 to 6 carbon atoms.

b) phenolic dicarboxamides having the general formula



in which

p is 0 to 6, preferably 2

q is 0 to 12, preferably 0 or 6

R₃ is hydrogen or alkyl with from 1 to 6 carbon atoms

R₄ is alkyl with from 1 to 6 carbon atoms, optionally together with

c) phenolic phosphites having the general formula



in which

- 10 R_5 is alkyl with from 1 to 6 carbon atoms and
 R_6 is hydrogen or alkyl with from 1 to 6 carbon atoms

Suitable phenolic dicarboxylates are:

- diethylene glycol bis(2-[3,5-diethyl-4-hydroxyphenyl] ethanoate); diethylene glycol bis(5-[3-isobutyl-4-hydroxyphenyl] pentanoate);
 15 triethylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate);
 octaethylene glycol bis(2-[3,5-di-tert.amyl-4-hydroxyphenyl] ethanoate);
 dipropylene glycol bis(3-[3,5-di-sec.butyl-4-hydroxyphenyl] propanoate);
 tripropylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate);
 tetrapropylene glycol bis(3-sec.pentyl-4-hydroxybenzoate);
 20 tributylene glycol bis(3-ethyl-5-tert.butyl-4-hydroxybenzoate);
 dipentylene glycol bis(2-[3-isopropyl-5-tert.amyl-4-hydroxyphenyl] ethanoate);
 dihexylene glycol bis(4-[3-cyclohexyl-4-hydroxyphenyl] butanoate); and the like. Preference is given to additives in which R_2 is an alkyl group that cause steric hindrance, e.g. isopropyl, t-butyl or t-amyl. In even more preferred additives each of R_1 and R_2 is a sterically hindering alkyl group. Most preferred phenolic
 25 dicarboxylates are triethylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate) and, tripropylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate).

Suitable phenolic dicarboxamides are:

- N,N'-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoyl) hydrazine;
 N,N'-bis(2-[3-methyl-5-tert.butyl-4-hydroxyphenyl] ethanoyl) hydrazine;
 30 N,N'-bis(3,5-isopropyl-4-hydroxybenzoyl) hydrazine; 1,1-bis(3-[3,5-di-isopropyl-4-hydroxyphenyl] propanamido) methane;
 1,3-bis(4-[3-{1-methyl-cyclopentyl}-4-hydroxyphenyl] butanamido) propane;
 1,5-bis(5-[3-isobutyl-4-hydroxyphenyl] pentanamido) pentane; 1,6-bis(3-sec.pentyl-4-hydroxybenzamido) hexane;
 35 1,6-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanamido) hexane;
 1,8-bis(6-[3-ethyl-5-tert.butyl-4-hydroxyphenyl] hexan-amido) octane;
 1,12-bis(2-[3,5-diethyl-4-hydroxyphenyl] ethanamido) dodecane; and the like. Preference is given to additives in which R_4 is an alkyl group that cause steric hindrance, e.g. isopropyl, t-butyl or t-amyl. In even more preferred additives each of R_3 and R_4 is a sterically hindering alkyl group. Most preferred phenolic
 40 dicarboxamides are N,N'-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoyl) hydrazine, and 1,6-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanamido) hexane.

Suitable phenolic phosphites are:

- tris(2-tert.butylphenyl) phosphite;
 tris(2-tert.amylphenyl) phosphite;
 45 tris(2,4-diethylphenyl) phosphite;
 tris(2-tert.amyl-4-tert.butylphenyl) phosphite;
 tris(2,4-di-isopropylphenyl) phosphite;
 tris(2-isopropyl-4-tert.butylphenyl) phosphite;
 tris(4-tert.butyl-2-isopropylphenyl) phosphite;
 50 tris(2-[1-methyl-cyclopentyl] phenyl) phosphite;
 tris(2-methyl-4-tert.butylphenyl) phosphite;
 tris(2,4-di-tert.butylphenyl) phosphite; and the like. Preference is given to additives in which R_6 is an alkyl group that cause steric hindrance, e.g. isopropyl, t-butyl or t-amyl. In even more preferred additives each of R_5 and R_6 is a sterically hindering alkyl group. Most preferred phenolic phosphite is tris(2-tert.butylphenyl)
 55 phosphite.

When selecting a phenolic dicarboxamide in which q is 5 to 7, it is beneficial to employ such additive in admixture with a phenolic phosphite, preferably in such a mixture the phenolic dicarboxamide and phenolic phosphite are present in about equal weight proportions, i.e. 1 pbw of a phenolic dicarboxamide per 0.8 to

1.2 pbw of a phenolic phosphite.

The additive can be added to the copolymer by conventional methods suitable for producing an intimate mixture of the copolymer and the additive without unduly degrading the copolymer or the additive. Such methods include dry blending of the additive and the copolymer in the finely divided form followed by hot pressing, coextrusion of the copolymer and the additive to thereby produce a stabilized composition as an extrudate, or by intimately mixing in a mixer or blender employing high shear.

The best mode of operating this invention is elucidated in the Example disclosed hereinafter.

Preferred copolymers are those having a weight molecular weight of at least 2000, better still, at least 6000.

The improved compositions of this invention can be processed into articles of manufacture such as fibres, sheets, films, laminates, containers, tubes, piping and articles having an intricate shape by conventional processing techniques such as melt-spinning, extrusion, coextrusion, blow-moulding, compression-moulding, injection-moulding and solid phase pressure forming. The invention is of special importance to melt-spinning, extrusion and coextrusion applications. In addition, it is of special importance to all those applications where adequate long-life stability of finished articles of manufacture is essential.

EXAMPLE

The following additives were tested on their thermostabilizing performance:

- 1) triethyleneglycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate),
- 2) N,N'-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoyl) hydrazine,
- 3) 1,6-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanamido) hexane,
- 4) tris(2,4-di-tert.butylphenyl) phosphite,
- 5) * octadecyl 3-(3,5-di-tert.butyl-4-hydroxyphenyl) propanoate,
- 6) * pentaerythrityl tetra(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate).

Test specimen having a length of 30 mm and a width of 3 mm were cut from a sheet which was prepared by compression-moulding at 250 °C from an ethylene/propylene/carbon monoxide terpolymer having an alternating structure, a crystalline melting point of 218 °C and an intrinsic viscosity of 1.6 dl/g (measured in meta-cresol at 60 °C).

The test specimen were subjected to aerobic oven aging tests at various temperatures, marked in the Table below. All specimen were bent by hand at an angle of 180° and the appearance of cracks was recorded as brittleness (failure). Time of heating in the oven to reach the moment of failure was determined.

Additives 1, 2 and 6 were employed in an amount of 0.5 %wt, additive 5 was employed in an amount of 0.3 %wt and additives 3 and 4 were employed as a mixture, each component being used in a concentration of 0.25 %w on the weight of the copolymer.

TABLE

Additive	Time to failure (hrs)		
	Heating at		
	135 °C	115 °C	105 °C
1	65	240	390
2	70	260	>500
3, 4	170	170	390
5*	17	90	210
6*	12	70	240

* for comparison

*for comparison

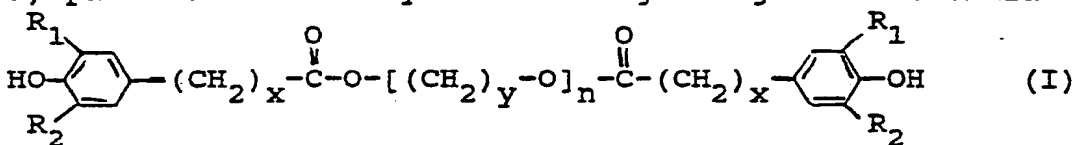
The table shows that additives 5 and 6 which are commercial top quality single thermostabilizers for polyethylenes, polypropylenes and polyamides completely fail to show an attractive performance, and since the polymer degradation mechanism of the relevant ethylene/carbon monoxide copolymers used in this invention and the physico-chemical behaviour of the additives in the copolymers are not known there is no way of predicting the favourable results obtained with the additives used in this invention.

Results at best similar to, but mostly inferior to those reported for the comparative additives in the Table hereinabove were obtained when testing many other commercial thermostabilizers for thermoplastics.

10 Claims

1. A stabilized composition comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and, based on the weight of the copolymer, from 0.03 to 5.0 %w to an additive selected from

a) phenolic dicarboxylates having the general formula



in which

x is 0 to 4

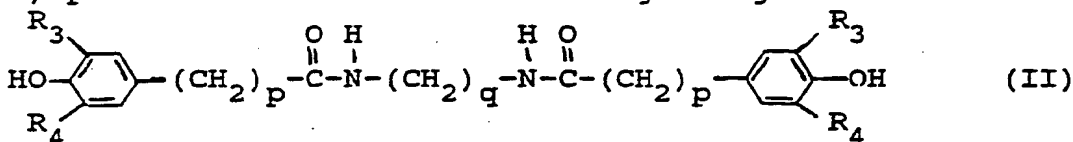
y is 2 to 6

n is 2 to 8

R₁ is hydrogen or alkyl with 1 to 6 carbon atoms

R₂ is alkyl with 1 to 6 carbon atoms.

b) phenolic dicarboxamides having the general formula



in which

p is 0 to 6

q is 0 to 12

R₃ is hydrogen or alkyl with from 1 to 6 carbon atoms

R₄ is alkyl with from 1 to 6 carbon atoms, optionally together with

c) phenolic phosphites having the general formula



in which

R₅ is alkyl with from 1 to 6 carbon atoms and

R₆ is hydrogen or alkyl with from 1 to 6 carbon atoms.

2. A composition as claimed in claim 1 in which x is 2.

3. A composition as claimed in claim 1 or 2 in which y is 2 or 3.

4. A composition as claimed in any one of claims 1 to 3 in which n is 3.

5. A composition as claimed in any one of claims 1 to 4 in which p is 2.

6. A composition as claimed in any one of claims 1 to 5 in which q is 6 or 0.

7. A composition as claimed in any one of claims 1 to 6 in which R₂, R₄ and R₅ are alkyl groups causing steric hindrance.

8. A composition as claimed in any one of claims 1 to 7 in which R₁, R₃ and R₆ are alkyl groups causing steric hindrance.

9. A composition as claimed in any one of claims 1 to 8, which comprises a mixture of 1 pbw of a phenolic dicarboxamide selected from group b) and from 0.8 to 1.2 pbw of a phenolic phosphite selected from group c), q having a value of from 5 to 7.

10. A composition as claimed in any one of claims 1 to 9 in which the copolymer is a copolymer of ethylene and carbon monoxide.

11. A composition as claimed in any one of claims 1 to 9 in which the copolymer is a copolymer of ethylene, propylene and carbon monoxide.



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 289 077
A3**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88200744.6

(51) Int. Cl.⁴: **C08K 5/13 , C08L 73/00 ,
/(C08L73/00,C08K5:13)**

(22) Date of filing: 19.04.88

(30) Priority: 29.04.87 GB 8710171

(43) Date of publication of application:
02.11.88 Bulletin 88/44

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

(66) Date of deferred publication of the search report:
07.02.90 Bulletin 90/06

(71) Applicant: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.**
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

(72) Inventor: **Schmitter, André, Dr.**
7 Rue des Alpes
F-68220 Hegenheim(FR)

(74) Representative: **Aalbers, Onno et al**
P.O. Box 302
NL-2501 CH The Hague(NL)

(54) **Thermostabilized copolymer composition.**

(57) A stabilized composition comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and, based on the weight of the copolymer, from 0.03 to 5.0 %w to an additive selected from phenolic dicarboxylates, and phenolic dicarboxamides, optionally together with phenolic phosphites.

EP 0 289 077 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 0744

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-3 929 727 (D. H. RUSSELL et al.) * abstract; example 3; claims *	1,10	C 08 K 5/13 C 08 K 5/20
A	US-A-3 948 832 (D. E. HUDGIN) * abstract; example 3; claim 1 *	1,10	C 08 K 5/52 C 08 L 73/00
A	US-A-3 968 082 (D. E. HUDGIN) * abstract; claim 1 *	1,10	
A	US-A-4 139 522 (P.R. LANTOS) * abstract; claim 1 *	1,10	
A	EP-A-0 094 092 (PHILLIPS PETROLEUM CO.) * whole document *	1	
A	US-A-4 120 846 (J. D. SPIVACK et al.) * abstract *	1	
A	US-A-3 878 149 (R. FISCHER et al.) * columns 5,6; formulas VII,IX *	1	
A	EP-A-0 209 127 (ADEKA ARGUS CHEMICAL CO. LTD.) * page 71, line 17 - page 72, line 17; claims 1,10 *	1	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 10-11-1989	Examiner HOEPFNER W.W.G.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			